



ON THE COHESIVE ENERGY AND CHARGE DENSITY OF URANIUM DIOXIDE

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Self-consistent band structure calculations have been used to calculate the cohesive energy of  $UO_2$ . The computed cohesive energy was 1.641 Ry/formula unit compared with an experimental value of 1.614 Ry/formula unit. The self consistent charge density has been compared with free atom charge densities to illustrate the formation of bonding charge between the atoms.

We have already reported<sup>1</sup> how *ab initio* energy band structure calculations were used to calculate the zero temperature equation of state of  $UO_2$  near the experimental lattice parameter. The theoretical value for the lattice parameter (or, equivalently, bond length) was in good agreement with experiment and the overall band structure corresponded to observations in photo-emission<sup>2,3</sup>, inverse photo-emission (BIS)<sup>4</sup> and optical<sup>5</sup> experiments. More recently inverse photo-emission in the UPS range<sup>6</sup> and angular dependent photo-emission experiments<sup>7</sup> have improved upon an already comprehensible picture of the electronic structure.

In principle it is possible to calculate other ground state properties, such as the cohesive energy, in the local density approximation<sup>8,9,10</sup>. The cohesive energy is a more formidable problem than the bond length since it is in general necessary to calculate the total energy of the isolated atoms, the total energy of the solid, and to take the difference. The total energies involved are very large - for actinides and their compounds more than 50,000 Ry - but the difference very small (< 1 Ry) and this makes it difficult to obtain the required accuracy. Such calculations have been successful for lighter metals<sup>11</sup> but even very small numerical errors in the self-consistent charge density of an actinide core can lead to errors in the total energy larger than the cohesive energy. One scheme to avoid the large total energies has been suggested by Gunnarsson et al.<sup>12</sup>, and implemented for light molecules<sup>13</sup>, semiconductors<sup>14</sup>, and the light actinide metals<sup>15</sup>. In this scheme the frozen core approximation is used and only that part of the energy which changes with a change of the valence charge density is computed. This valence energy is not the energy of the valence electrons, which is anyway not separable from the total energy

because of two-particle interactions, but it is a suitable small quantity (of less than 50 Ry in  $UO_2$ ) which makes an *ab initio* calculation of the cohesive energy of  $UO_2$  possible. We have used this scheme in the present work.

One of the successes of the ionic approximation<sup>16</sup> for  $UO_2$  is that the lattice energy is given correctly<sup>17</sup>. A recent discussion of the model has been given by Catlow<sup>18</sup> who quoted the following data:

Heat of formation of $UO_2$	H = -825 mRy
Molar sublimation energy of U	S = 372 mRy
Dissociation energy of $O_2$	D = 379 mRy

This list actually exhausts the experimental data, however the lattice or separation energy, L, is derived from the Born Haber cycle

$$H = S + D + I + A - L \quad (1)$$

where I is the difference in energy between a  $U^{4+}$  ion and a neutral uranium atom (sum of the first four ionization energies) and A is the sum of the first and second electron affinities of oxygen. Neither of these quantities has been measured but a knowledge of both is required to determine L. A is normally estimated by fitting other Born Haber cycles involving oxygen and Catlow<sup>18</sup> estimated

$$A = 573 \text{ mRy}$$

I was taken from Dirac-Fock calculations<sup>19</sup> (5.069 Ry) and 235 mRy was added to allow for correlation energy. The lattice energy from the Born Haber cycle was then 7.791 Ry compared with 7.622 Ry calculated from the ionic model<sup>18</sup>. The 235 mRy correlation energy is entirely empirical. A grasp of the kind of accuracy to be expected from the atomic calculations may be obtained from the list of calculated ionization energies given in Schoenes<sup>20</sup>.

recent review of  $UO_2$ . There is agreement between different calculations of  $I$  to within about  $.4 \text{ Ry}^{21}$ . There are also doubts about  $A^{18}$  but the total errors in  $L$  from the Born Haber cycle seem unlikely to be greater than 10%. However we note that  $L$  is never measured. It is also very large compared with the measured quantities  $H, S, D$ . If errors were made in the description of the chemical bond, such as the neglect of partial covalency, the errors in energy would appear as moderately sized quantities in the heat of formation, being of the order of  $.3 \text{ Ry}$ , and as small quantities in  $L$ . When self-correcting tendencies<sup>22</sup> of the ionic approximation are also considered it appears that the good results for the lattice energy are a less than sensitive indicator of how charge is really distributed.

The band structure description provides a value for the difference in energy between the solid and corresponding neutral free atoms

$$E_c = S + D - H \quad (2)$$

where  $E_c$  is the cohesive energy in this case. All of the quantities on the right hand side of (2) have been measured and, from the data given above, the experimental value for  $E_c$  is  $1.576 \text{ Ry}$ . A more recent value for  $S$  is  $410 \text{ mRy}^{23}$  yielding  $E_c = 1.614 \text{ Ry}$ .

The LMT0-ASA<sup>24</sup> band calculations were made as described previously except that a larger size for the uranium Wigner-Seitz sphere ( $3.12 \text{ a.u.}$ ) was chosen together with a corresponding smaller size for the oxygen spheres ( $2.61 \text{ a.u.}$ ). The uranium sphere radius was then quite close to that of the Wigner-Seitz radius in uranium metal. We have found that this prescription<sup>25</sup> works quite well for actinide  $NaCl$  compounds and it leaves no free parameters in the calculation. In addition we included oxygen  $d$ -states in the basis set whereas an  $sp$  basis was used in our earlier calculations. Previously we omitted the  $f$ -states, which are on the low density side of a Mott transition, from the band structure calculations<sup>1</sup>. We have now improved upon this treatment. Firstly the  $f$ -states were treated as band states. The Fermi level then lay in the  $f$ -band and the system was metallic. The equation of state is shown in fig.1. where we have also shown the  $f$ -contribution. The theoretical equilibrium lattice parameter ( $9.1 \text{ a.u.}$ ) corresponds to a volume about 35% too small. This is seen to be due to the attractive  $f$ -contribution in the equation of state. Next we noted that spin polarized band calculations of half-filled or almost half-filled bands give the correct volume for Mott Insulators<sup>25,26,27</sup>. Here a half-filled band becomes a filled spin up band when the moment saturates. This corresponds to the understanding that the many electron state of a filled band can equally well be written in terms of a set of Wannier functions centred at the atomic sites<sup>28</sup>. In order to reproduce this effect for a band with two  $f$ -electrons we place  $1/7$  of an electron in each  $f$ -state. This fills the  $f$ -bands with a total of two electrons. Thus the single-particle  $f$ -band states are not filled to the Fermi level as is usual in band calculations but we have achieved the desired objective of

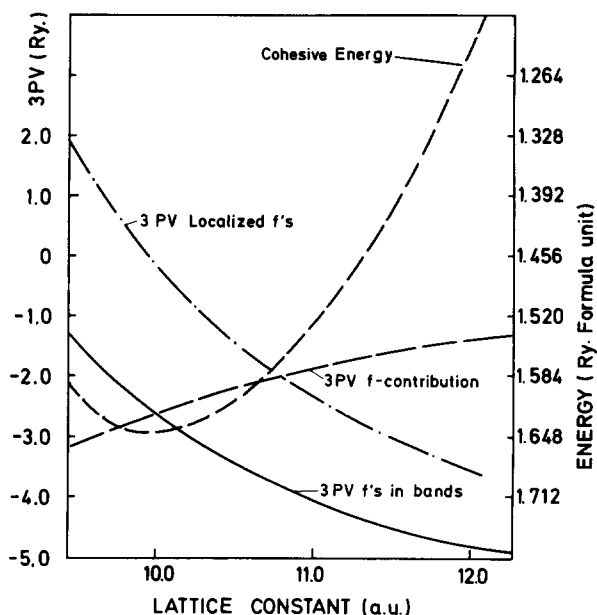


Fig.1. The zero temperature equation of state and cohesive energy of  $UO_2$ . The left and right ordinates are for the equation of state and cohesive energy, respectively.

- equation of state with itinerant  $f$ -electrons
- ..... itinerant  $f$ -electron contribution
- ..... equation of state with localized  $f$ -electrons
- energy curve

Lattice parameter is in atomic units  
( $1 \text{ a.u.} = .5292 \text{ \AA}$ )

a localized many electron state. This device has been successfully applied to several cerium compounds and will be reported more fully elsewhere<sup>29</sup>. The resulting equation of state is shown in fig.1. The theoretical equilibrium lattice parameter is correct to within 4% and the  $f$ -pressure has almost vanished ( $(3PV)_f = 10 \text{ mRy}$ ). Hybridization between single particle  $f$ -states and other states is now included, and leads to a small amount of  $f$ -character in the valence band - as observed in photo-emission experiments<sup>2,3</sup>. There is, nevertheless, no significant  $f$ -bond.

The valence energies for the free atoms and solid  $UO_2$  at the equilibrium volume are shown in table 1. The atomic calculation for oxygen was spin polarized. The magnetic energy of uranium should not change appreciably from atom to solid for a given configuration. However, the ground states of the free atom and solid are  $f^3$  and  $f^2$ , respectively. Therefore there is a change of magnetic energy equal to the difference in spin polarization energy between  $f^2$  and  $f^3$  configurations - this is calculated to be  $51 \text{ mRy}$ .

The total cohesive energy was thus found to be  $1.641 \text{ Ry}$ . This is in very reasonable agreement with experiments.

TABLE 1

Valence energy of oxygen x2	= -28.21 Ry
Spin polarization energy O x 2	= -.24 Ry
Valence energy of uranium	= -14.81 Ry
Spin polarization energy U( $f^3d^1s^2$ )-U( $f^2d^2s^2$ )	= -.05 Ry
Total	-43.31 Ry
Valence energy of $UO_2$ at equilibrium volume ( $a=10$ a.u.)	-44.95 Ry
Difference	1.64 Ry

List of valence and spin polarization energies involved in the cohesive energy of  $UO_2$  (1 Ry/formula unit = 312 kcal/mole).

The radial charge densities ( $4\pi r^2\rho$ ) of U and O in  $UO_2$  are plotted in fig.2. For comparison we have also shown the radial charge densities of the free neutral atoms ( $f^2d^2s^2$  for U) and of a free  $U^{4+}$  ion. The integral of the charge density in the solid is also graphed as a function of radius and it may be seen that there is a total of about 4 electrons in the U sphere for the sphere size that we have chosen but only two inside a radius of 1.85 a.u. which is very close to the ionic radius, 1.89 a.u.<sup>30,31</sup>, of  $U^{4+}$ . However the radial dependence of the charge density of U in the solid is not identical to that of  $U^{4+}$ , even inside a radius of 1.85 a.u., and the difference between the two increases with radius. For the sphere size chosen O is approximately a  $1^-$  ion and bonding charge has formed in the outer region of both anion and cation spheres.

A free oxygen atom does not bind a second additional electron, a property which it retains in the solid. The suggestion<sup>18</sup> that the electron is bound by the Madelung potential is incorrect. The Madelung contribution to the electronic potential is independent of radius and changes the eigenvalues without modifying the wave functions. This has produced severe theoretical difficulties in the description of oxygen valence states in solids<sup>32</sup>. Band structure calculations resolve these difficulties in a consistent manner since they describe the radial redistribution of charge quite naturally. A complete comparison of the different theoretical models of the electronic

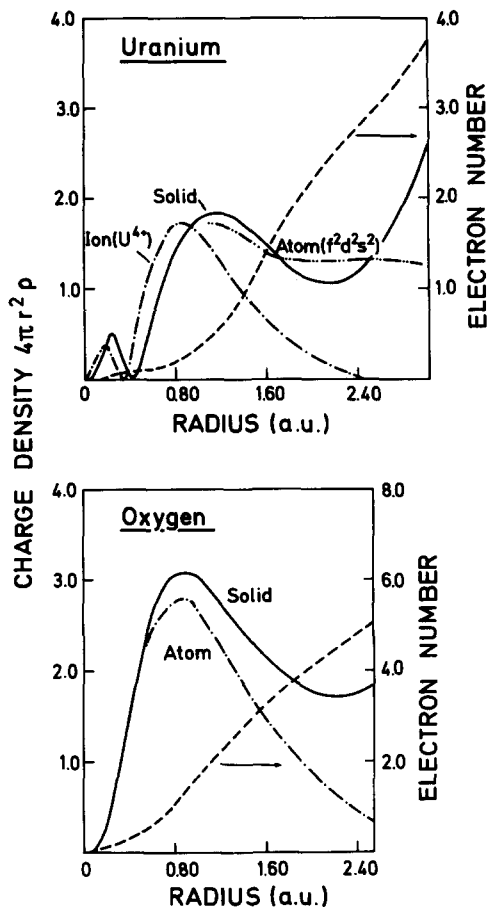


Fig.2. Radial charge density ( $4\pi r^2\rho$ ) of uranium and oxygen in the solid and as free atoms

- charge density in the solid
- - - integral of charge density in the solid (electron number)
- · - charge density of O atom and the  $U^{4+}$  ion
- · · charge density of U( $f^2d^2s^2$ ) atom

structure of  $UO_2$  should include a study of the shear properties which are particularly sensitive to directional bonding charge<sup>31</sup>. Since we have used spherical potential throughout we have not yet attempted this. However, we have found that band structure calculations describe the isotropic cohesive properties satisfactorily.

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